

HIGH TEMPERATURE PROTECTIVE
COATINGS FOR REFRACTORY METALS

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By E. B. Bitzer, J. Rexer, and R. G. Fenish

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SUMMARY

20790

A program was initiated to establish the feasibility of using iridium as a protective coating for unalloyed columbium and tantalum. Interest in iridium stemmed from the observation that this metal provided remarkable protection to graphite at temperatures of 2000°C.

The program encompasses a study of methods of applying iridium to the refractory metal substrate, investigation of the chemical and mechanical compatibility of the coating-substrate system, and limited oxidation studies.

Electrodeposition of iridium on the substrate appears the most promising method of sample preparation. The first quarter was devoted to equipment construction and establishing plating parameters. Study of the effect of chemical interaction on the mechanical behavior of the coating-substrate systems was initiated using roll bonded, pressure bonded, and refractory metal plated samples of iridium. A microbend test was used to observe continuously the microstructure of coated samples loaded to fracture.

INTRODUCTION

Author ↑

Improved protective coatings for the refractory metals are needed for many high temperature applications. The life provided by available coatings is too brief to take full advantage of the strength and temperature capabilities of the refractory metals.

Our approach to the coating problem stems from the discovery that iridium provides remarkable protection for graphite at temperatures to 2000°C.⁽¹⁾ This coating might protect the refractory metals from oxidation at high temperatures. Iridium has the necessary oxidation resistance, but its behavior when in contact with a refractory metal substrate is unknown.

A program was initiated to establish the feasibility of employing iridium as a protective coating on unalloyed columbium and tantalum. Effort is being concentrated in three areas: 1) methods of applying iridium to the refractory metal substrates, 2) studies of chemical and mechanical compatibility of the coating-substrate systems, and 3) oxidation studies. Electrodeposition of iridium on the substrates from fused salts appears the most promising coating method; but other methods, such as roll bonding, will be examined to insure that our evaluation is representative of the coating-substrate system. The mechanical properties of the substrate may be harmed by chemical interaction of the coating and substrate. The diffusion zones which develop with time at high temperature will be examined to establish whether or not a diffusion barrier is required. The effect on chemical interaction in the oxidation behavior of the iridium coating will be noted.

This report describes progress made during the first quarter, October 23, 1964, to January 23, 1965.

BACKGROUND

Interest in the platinum group metals as protective coatings for refractory metals was aroused when, under an Air Force sponsored contract⁽¹⁾ in our Laboratory, iridium was found impervious to the diffusion of oxygen at temperatures in excess of 2000°C. Later, a thin metal cladding of iridium protected graphite in an oxidizing plasma torch test under sonic and supersonic (Mach 3.5) conditions at a temperature of 2150°C for 20 minutes. The entire platinum group family was reappraised as a coating for refractory metals, and iridium was established as the most promising candidate. Oxidation behavior, oxygen permeability, and chemical and mechanical compatibility with substrate refractory metals were studied.

Oxidation

Published data for the oxidation of the platinum group metals are reported in the form of the linear rate of weight change (in mg/cm²/hr) as a function of temperature.^(2, 3) At high temperatures, this weight loss is associated with the formation of a volatile oxide, causing a recession of the surface. For

our purposes, where we are considering the platinum group metals as protective coatings on the refractory metals, the rate of recession (in mils/hr) is a more meaningful criterion. We have, therefore, recalculated the published data on this basis and plotted the results in Figure 1.

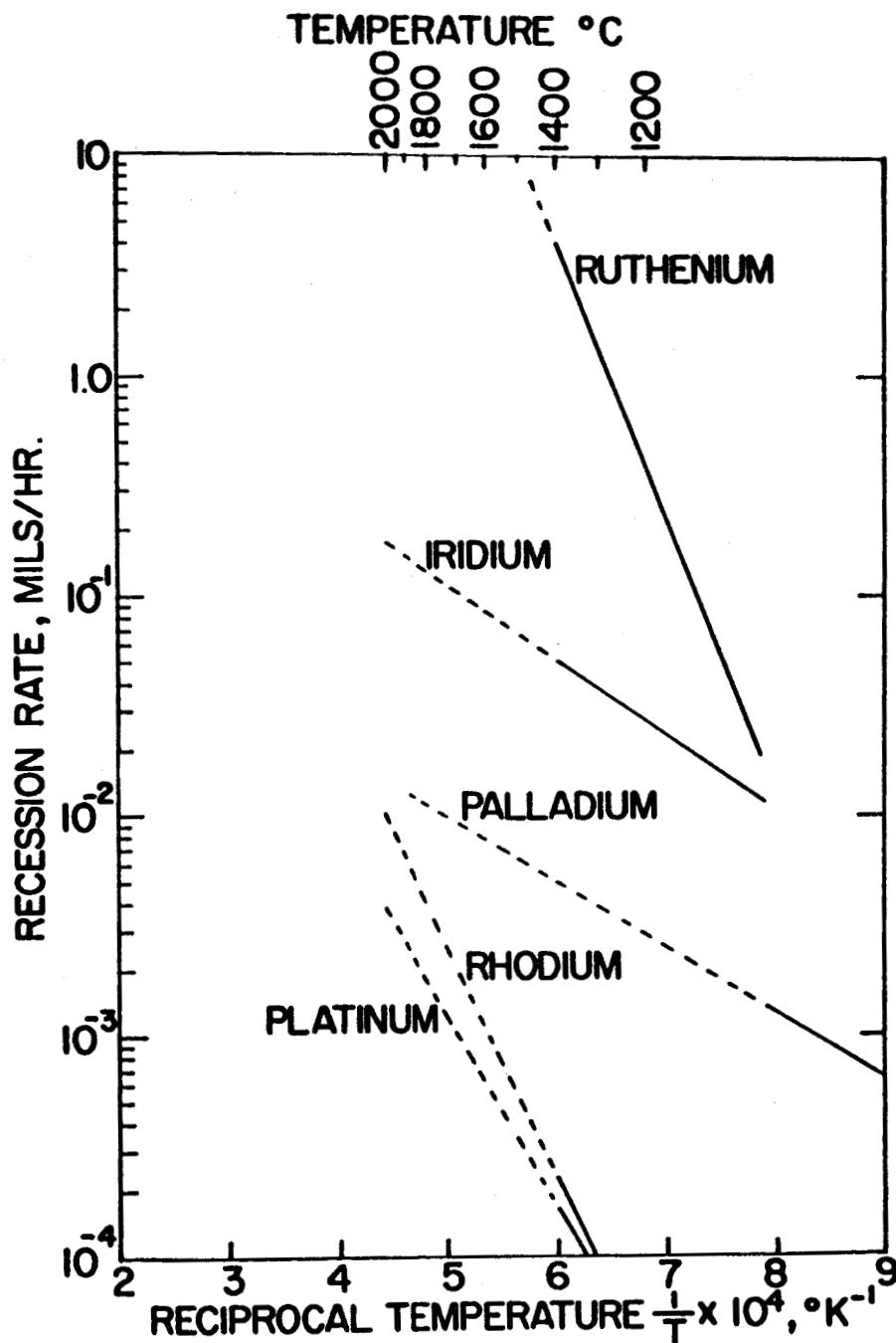


Figure 1. Oxidation Rate Data for the Platinum Group Metals Exposed to Slowly Moving Air at One Atmosphere Pressure. N-6483

These data, which are for oxidation in slowly moving air at one atmosphere, show (by extrapolation) that platinum, rhodium, palladium, and iridium recess at rates of less than 0.1 mils/hr at temperatures to 2000°C. The high recession rates of osmium and ruthenium combined with the toxic nature of their oxides make these metals unpromising candidates.

The recession rate of the platinum group metals in the temperature range of interest is affected by gas velocity.⁽²⁻⁵⁾ At low velocities, the reaction is limited by diffusion of either oxygen to the metal or volatile oxides away from the metal through a boundary layer of reactants and products. With increased gas velocity, the thickness of the boundary layer is reduced, and the reaction rate increases. The maximum rate is governed by the rate of reaction on the surface of the metal. Reported data for the effect of gas velocity on recession rates are not in quantitative agreement,⁽²⁻⁵⁾ but they do bear out the general behavior described above. On the basis of available data, one might expect an increase in recession rate of at least one order of magnitude at high gas velocities and atmospheric pressure.

The recession rates of the platinum group metals decrease with decrease in oxygen partial pressure. Fryburg and Petrus⁽⁶⁾ have shown that this applies for the case of platinum at temperatures between 900° and 1500°C and at pressures between 15 microns and one atmosphere; other investigators have considered the dependence on oxygen partial pressure for the various platinum group metals.⁽²⁾ Recent work in the Parma Laboratory⁽¹⁾ under Air Force Contract AF 33(657)-11253 has shown a linear decrease in the recession rate of iridium with decrease in oxygen partial pressure at a temperature of 1181°C. (See Figure 2.) It is of particular interest to note that this behavior is in sharp contrast to the performance of silicide coatings which lose their protective nature under conditions of reduced pressure.⁽⁷⁾

Most investigators have studied the oxidation behavior of the platinum group metals under dry conditions, but a limited amount of data indicates that the presence of water vapor does not have an adverse effect on the oxidation resistance. Experiments on platinum at 1200° and 1400°C in wet and dry air showed no significant difference in oxidation rate.⁽⁵⁾ Our work⁽¹⁾ on iridium has shown no effect of water vapor at 1160°C.

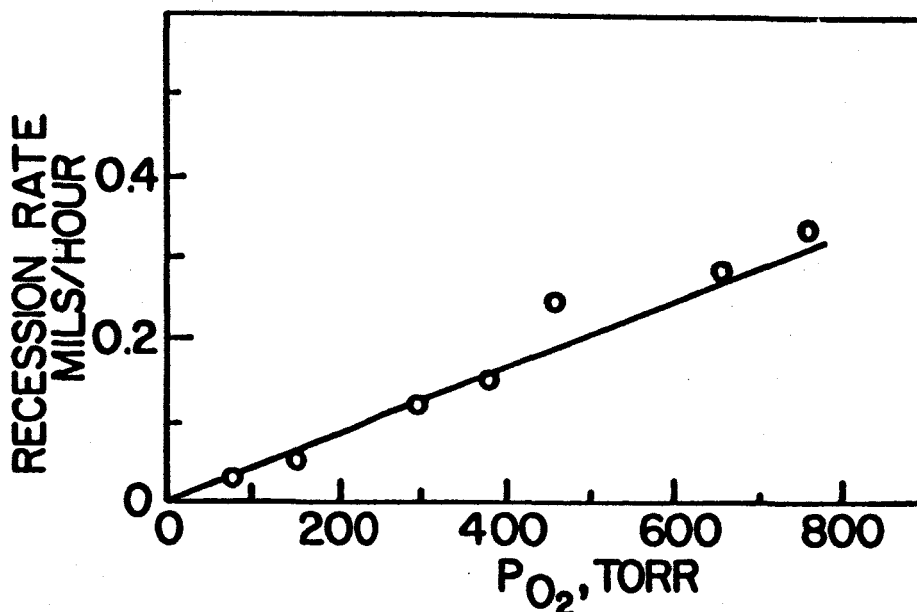


Figure 2. The Effect of Oxygen Partial Pressure on the Oxidation Rate of Iridium. Temperature 1181°C, Flow Rate 48 mils/min/cm². N-6484

Oxygen Permeability

Permeability is best described by the permeability constant, $P \cdot l$, where P is the permeability and l is the thickness. This quantity is related to the diffusion coefficient by the equation:

$$P \cdot l = -D \, dc,$$

where D is the diffusion coefficient and dc is the concentration variation.

Iridium appears to exhibit the lowest permeability of the platinum group metals. Experiments have been conducted on the permeability of iridium to oxygen at temperatures between 1075° and 2200°C at an oxygen partial pressure of 50 torr. ⁽¹⁾ No oxygen permeability was detected, and the value of the permeability constant as defined by the precision of the technique is less than 3.5×10^{-15} g/cm/sec. We have also studied the permeability of rhodium to oxygen at temperatures from 1300° to 1550°C at 50 torr oxygen and have found the permeability constant to increase from 3×10^{-14} to 5×10^{-12} g/cm/sec over this temperature interval. ⁽¹⁾ An investigation of platinum permeability to oxygen resulted in no permeability at 1400°C to the limit of detection, yielding a value for the permeability constant below the order of 10^{-15} g/cm/sec. ⁽⁸⁾

Studies have not been made on ruthenium, but it is expected to have a low oxygen permeability as a member of the platinum group. Palladium, however, which has a higher solid solubility for oxygen than the others in the group, is permeable to oxygen at 1400°C;⁽⁹⁾ a quantitative determination of the permeability constant has not been made.

The significance of the low permeability constant found for several of the platinum group metals can be seen quite readily by a calculation of the time required for oxygen to penetrate a protective coating and raises the oxygen content in the substrate to a level which causes embrittlement. If a 5-mil coating of iridium is employed and if one assumes that an increase of 500 ppm of oxygen in a 10-mil thick layer of a columbium substrate would be catastrophic, it is calculated that 8×10^8 hours would be required for transporting this amount of oxygen at temperatures to 2200°C. Obviously, the iridium-columbium system would be degraded in a very much shorter time because of oxidation of the iridium coatings and interdiffusion of the coating and substrate, but it should be clear that several of the platinum metals are highly impermeable barriers to oxygen.

Impurities may significantly alter the permeability. Betteridge and Rhys⁽¹⁰⁾ found that platinum alloys containing more than approximately 2 per cent molybdenum or tungsten in solid solution oxidized intergranularly and that the depth of penetration increased with increased alloy addition. Since the rate of diffusion of oxygen in unalloyed platinum is negligible, this result indicates that the rate is affected by the presence of the alloy addition. Buchinski and Girard⁽⁵⁾ suggest that the limited ability of platinum or platinum-20 per cent rhodium to protect a columbium base alloy, FS-85, is associated with very small amounts of the substrate diffusing through the coating, establishing a rapid inward diffusion path for oxygen. Metallographic examination indicates oxygen penetration creating localized areas of oxidized substrate metal, which results in blisterlike eruptions. As discussed later, this effect may be expected to be less pronounced with iridium.

Chemical Compatibility with Refractory Metals

Most of the binary phase diagrams of interest for the systems formed between the platinum group and the refractory metals are known. Of special concern is the minimum melting point of a given alloy system, since this temperature places an upper limit on the potential service temperature and also gives a rough idea of the relative amounts of solid state interdiffusion at elevated temperatures. The lowest melting point for the various binary systems of interest are included in Table I. It will be noted that iridium provides the highest minimum melting temperature with each of the four refractory metals.

TABLE I
INTERDIFFUSION OF PLATINUM GROUP METALS
WITH REFRACTORY METALS

Coating	Interdiffusion Zone Thickness* (ΔX) and Minimum Melting Point of Couple							
	Columbium		Molybdenum		Tantalum		Tungsten	
	Minimum Melting Point °C	ΔX Microns	Minimum Melting Point °C	ΔX Microns	Minimum Melting Point °C	ΔX Microns	Minimum Melting Point °C	ΔX Microns
Iridium	1840	50	2080	90	1950	40 (40)**	2305	50 (30)**
Ruthenium	1774	No data	1945	No data	1950(?)	45	2205	50 (40)**
Rhodium	1500	Above eutectic temp.	1940	115	1740	No data	1966	50 (60)**
Platinum	~1700	Above eutectic temp.	1769	No data	~1600	Above eutectic temp.	1769	110

* Four hours at 1700°C

** Three hours at 1800°C

Passmore⁽¹¹⁾ studied the interdiffusion at 1700° and 1800°C between the refractory metals and several barriers selected from the group Re, Os, Ru, Ir, Hf, Rh, V, Cr, Zr, and Pt. An inverse relationship was suggested between the extent of interdiffusion and the minimum solidus temperature. Ruthenium and iridium were noted as promising barriers for molybdenum and tungsten. At 1700°C, a temperature which exceeds the service temperature of existing columbium base alloys, iridium and columbium interdiffused to a depth of only 50 microns in four hours. Under the same conditions, iridium and tantalum interdiffused to a depth of 40 microns. Interfacial hardness for the latter two couples was considerably greater than that of either metal, a condition which raises the possibility of a brittle layer. The extent of interdiffusion was determined by Passmore between the platinum group metals and the refractory metals. (See Table I.)

Mechanical Compatibility with Refractory Metals

A successful coating must be adherent to the substrate and retain this adherence under conditions of thermal gradients and thermal cycles. A good match in expansion characteristics minimizes the stresses developed upon heating and cooling, avoids spalling of the coating, and distortion of the structure. The thermal expansion data for the platinum group and the refractory metals are plotted in Figure 3. Iridium has the lowest expansion of the three platinum group members and columbium the highest of the refractory metals, with the iridium-columbium system offering the closest match. Couples of iridium with tantalum, molybdenum, and tungsten become progressively poorer matches as do systems using platinum or rhodium.

Adherence may be retained in the face of a thermal expansion mismatch if the coating is capable of plastic flow. This behavior can be expected for most metallic coatings because of their inherent ductility. Buchinski and Girard⁽⁵⁾ noted no evidence of degradation as a consequence of severe thermal cycling of a molybdenum alloy (TZM) and a columbium alloy (FS-85) coated with platinum and with a platinum-10 per cent rhodium alloy. A similar observation has been made in our own Laboratory with an iridium coated-tungsten sample.

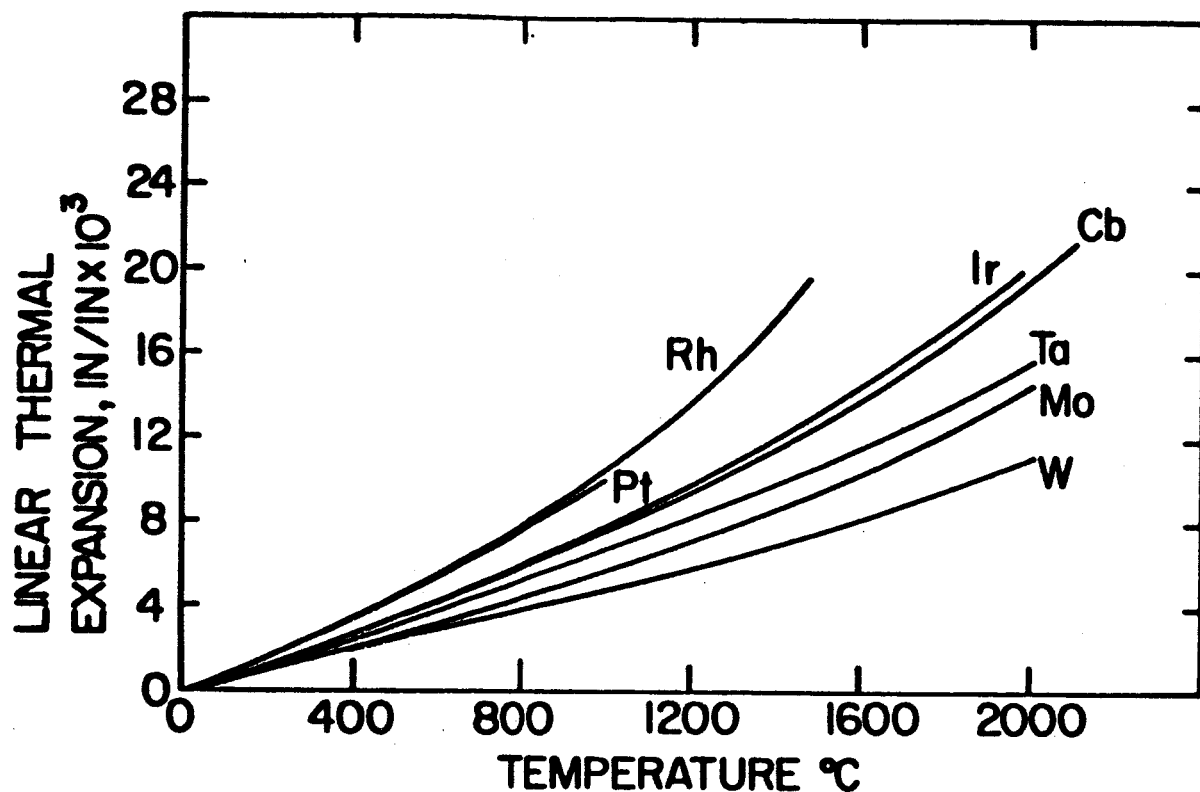


Figure 3. Thermal Expansion of the Platinum-Group Metals and the Refractory Metals. N-6485

Iridium the Best Candidate

The foregoing information leads to a selection of the most promising candidate from the platinum-group metals as follows:

Oxidation -

Osmium and ruthenium may be ruled out on the basis of their relatively high oxidation rates and oxide toxicity. The oxidation resistance of platinum, rhodium, and palladium exceeds that of iridium.

Permeability -

Iridium appears to have the lowest permeability to oxygen; but all of the platinum-group metals, with the probable exception of palladium, have low permeabilities. Impurities and diffusion alloying which detract from the permeability of platinum are less likely to occur with iridium because of its better chemical compatibility with the refractory metals.

Chemical Compatibility - Iridium has the highest minimum melting temperature with each of the refractory metals and yields the narrowest diffusion reaction zone in binary couples with the refractory metals.

EXPERIMENTAL

Sample Preparation

Emphasis was placed on preparing iridium-coated samples by electro-deposition from a fused salt. To support this work and provide assurance that a "representative" coating-substrate system would be examined, samples also were prepared by roll bonding, pressure bonding, and by electrodeposition of columbium on iridium and tantalum on iridium.

Fused salt electrodeposition of iridium. - The technique developed by Withers and Ritt⁽¹²⁾ to deposit iridium from a molten salt on nickel and/or gold was followed. Criscione et al.⁽¹⁾ in our Laboratory have modified this technique to plate directly on graphite. The feasibility of direct plating on each of the refractory metals also has been successfully demonstrated.

The experimental apparatus used for depositing iridium from a salt bath, consisting of 70 w/o sodium cyanide and 30 w/o potassium cyanide, is shown in the accompanying schematic. (Figure 4.) The recrystallized alumina crucible used to contain the molten salt measured about 3 1/2 inches outside diameter by 6 inches high. The alumina crucible was surrounded by a stainless steel jacket, watercooled at the top. Granulated alumina was placed between the alumina crucible and steel jacket and between the steel jacket and furnace.

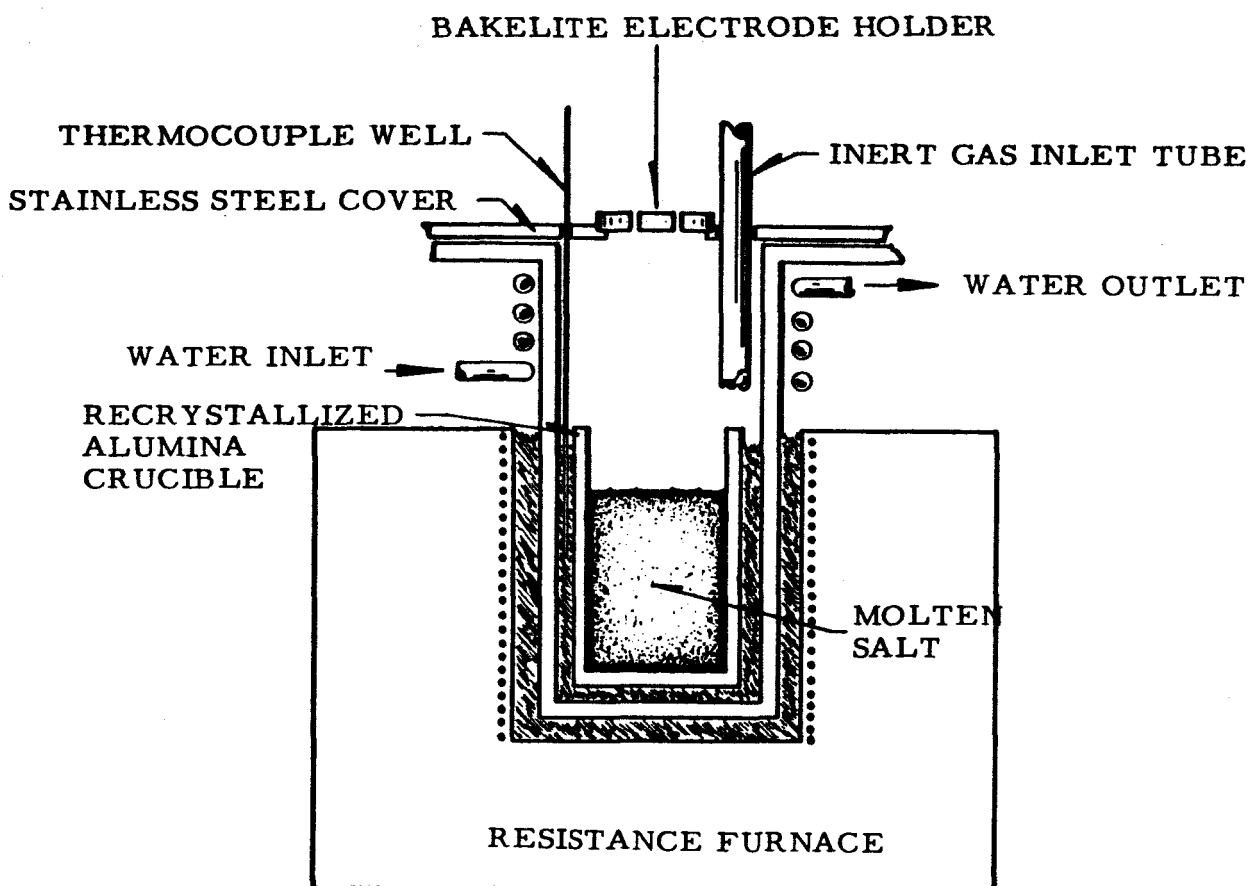


Figure 4. Schematic of Iridium Electrodeposition Apparatus.
(Not to Scale) N-6711

Initially, the cell was operated with the bath exposed to the atmosphere. Later, to prevent oxidation and moisture pickup, an argon atmosphere was maintained inside the stainless steel enclosure. The temperature of the bath was determined by means of a Chromel-Alumel thermocouple positioned between the alumina crucible and steel enclosure. Heating of the Hoskins pot furnace was regulated with a Variac, and the molten bath temperature was maintained between 600° and 650°C while plating.

The anodes for the molten salt bath consisted mainly of strips of iridium about $\frac{3}{8}$ inch wide by 20 mils thick. The cathodes were 20 mil-sheet tantalum and columbium ranging in size from $\frac{1}{4}$ inch to $1\frac{1}{2}$ inches wide by $1\frac{1}{2}$ inches to $2\frac{1}{2}$ inches long. Both the anodes and cathodes were held in position in the bath by means of graphite rods. The rods in turn were held in position by a piece of Bakelite through which they were inserted. The Bakelite was supported and centered above the bath by the stainless steel enclosure cover.

A power source capable of supplying direct current of 10 to 1000 ma was used. The cathode current density was usually held between 10 to 20 amp/ft², but at times it was raised to 20 to 40 amp/ft². To charge the molten bath with iridium, alternating current was first passed through two iridium electrodes for a day or two. Then the process of conditioning the bath and plating metal on the cathode was started. Since the anode efficiency always tended to be much higher than the cathode efficiency, the bath was also being charged with iridium during the conditioning treatment. The concentration of iridium in the bath was not determined analytically, since the quality of the coating should improve with increased iridium concentration in the bath. The cathodes used while conditioning the bath were either graphite rods or sheets of copper. As soon as a satisfactory coating was obtained, columbium or tantalum cathodes were placed into the bath.

Adherence can be strongly influenced by surface preparation. Our preparation has consisted of sanding the columbium or tantalum on 240, 400, and, finally, on 600 grit wet silicon carbide paper. The cathodes were then either washed in acetone and air dried or anodically etched in a concentrated sodium hydroxide solution at room temperature, washed with distilled water, and, finally, air dried.

Other methods of sample preparation. -

Roll and pressure bonding: Roll bonding of iridium to tantalum and columbium was performed using the Stellite Division facilities at Kokomo, Indiana. The substrates, 0.020 inch x $\frac{1}{4}$ inch x 1 inch, and iridium overlay, 0.010 inch x $\frac{1}{4}$ inch x 1 inch, were sandwiched in a Hastelloy alloy X "can" which was evacuated and welded. Alumina was sprinkled between the Hastelloy can and the specimens to prevent bonding of the sample to the "can."

Two "cans" were prepared, each containing an iridium-tantalum composite and an iridium-columbium couple. Rolling was done at 1200°C with reheats after each pass through the mill. A single rolling direction was maintained. One "can" was reduced 25 per cent in thickness and the other 35 per cent. The rolled bonded samples were carefully cut from the "can"; both appeared tightly bonded.

A single attempt was made to bond a sheet of iridium to tantalum and columbium by clamping and heat treating. The fixture used was similar to that described by Passmore⁽¹¹⁾ but was machined from unalloyed molybdenum.

Electrodeposition of refractory metals: Several samples of ten-mil iridium sheet were plated with either columbium or tantalum by the techniques developed by Mellors and Senderoff.^(13, 14) Dense coherent deposits of the refractory metals were formed by the electrolysis of a molten fluoride bath. The coated samples of iridium did provide excellent samples for study of interfacial behavior.

Sample Evaluation

To provide a better understanding of failure modes than can be gained from a simple bend test and to conserve material until coatings are considered representative, a fixture was constructed to allow direct observation of microstructure as a bending stress was applied to a coating-substrate system. The microbend test, first proposed by Flinn and Trojan,⁽¹⁵⁾ involves bending a small specimen, approximately $0.025 \times \frac{1}{8} \times 1$ inch, in the fixture shown in Figure 5 while viewing the metallographically prepared surface with a microscope. The entire stress gradient is visible, from maximum tension on the outer fibers to maximum compression on the surface butting against the center loading pin.

A fixture is being constructed to conduct conventional bend tests. The mechanical compatibility of coated specimens will ultimately be evaluated using this fixture; thermal cycling will also be employed. These tests should be performed not only on as-coated material but also on material after it has been exposed to elevated temperatures in order to reveal chemical compatibility.

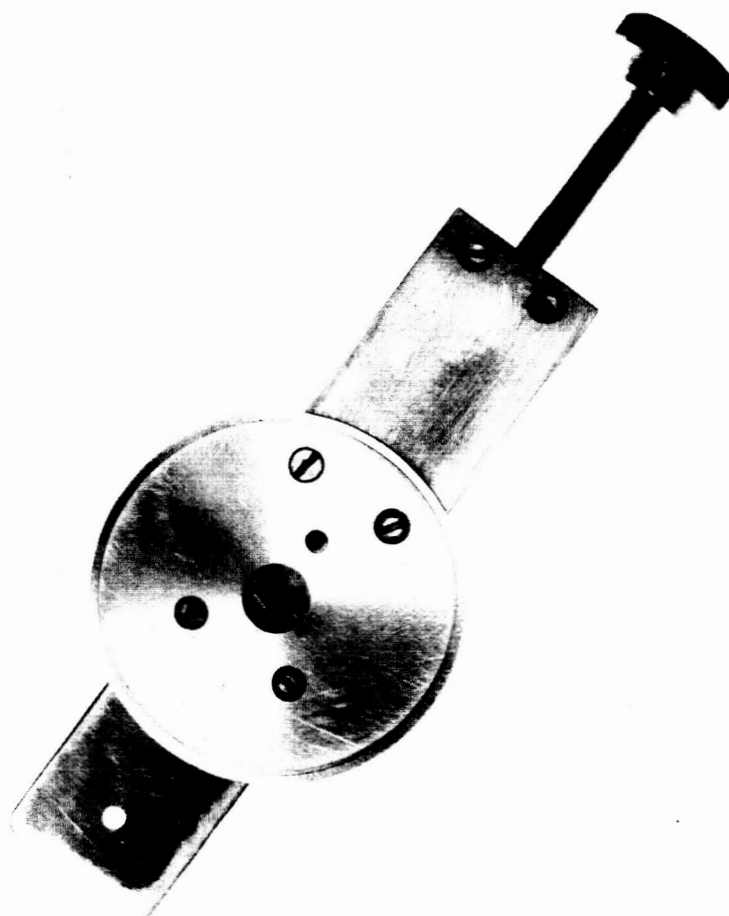


Figure 5. Microbend Fixture. N-6513

PROGRESS

Electrodeposition of Iridium

Initial experiments in which the fused salts were contained in a nickel crucible failed to deposit any iridium. The nickel crucible was felt to be a major source of contamination, and a second cell was activated which had previously been successfully employed under another program.⁽¹⁾ This cell used an Alundum crucible to contain the molten salt. After several days of conditioning, this cell produced an adherent, bright coating about 0.5 mil thick on columbium and tantalum cathodes. In subsequent attempts at plating, no deposits were produced.

Cell No. 2 was recharged with fresh salt, and the cell design modified as shown in Figure 4 to incorporate a cover as a means of introducing an argon atmosphere over the molten bath. In addition, a new large-capacity cell, No. 4, was constructed of similar design.

To date, neither of the latter cells has reproducibly yielded adherent coatings. Intermittently good deposits have been produced in Cell No. 4, but deposition rate has varied unaccountably from 0.24 mil/hr to 0.02 mil/hr under identical operating conditions.

Iridium deposited on copper was usually light gray, of satin finish, and quite smooth, whereas the deposits on columbium and tantalum were always dull, dark gray, and rough. A sheet of copper which had an iridium coating 0.9 of a mil thick was bent several times by hand through an angle of 180 degrees. The coating did not break away from the substrate and, with the unaided eye, no signs of cracking were evident.

A 2-mil iridium coating was applied to a sample of tantalum and a 1.7-mil iridium coating was applied to a columbium sample. The iridium coating flaked from both the columbium and tantalum substrates adjacent to the saw cuts when attempts were made to cut strips $\frac{1}{8}$ inch wide from the coated sheets with a diamond saw. When the specimens were stressed using the microbend tester, the iridium coating on both substrates cracked when the bend angle was about five degrees. The coating always cracked on the tension side of the bend and broke away from the substrate material. A strip of the 20-mil-thick, as-received, iridium, $\frac{1}{8}$ inch wide by $1\frac{1}{8}$ inches long, was stressed in the microbend tester. When bent through an angle of about six degrees, a crack appeared that originated on the tension side of the test piece. The crack penetrated more than halfway through the 20-mil-thick specimen.

Columbium and Tantalum Plated Iridium

The bond interface between electrodeposited columbium and tantalum on iridium was examined metallographically both in the as-deposited condition and after exposure at elevated temperatures. Figures 6 and 7 show the clean, void-free interface between the as-deposited refractory metal and the iridium substrate.

Ta

Ir

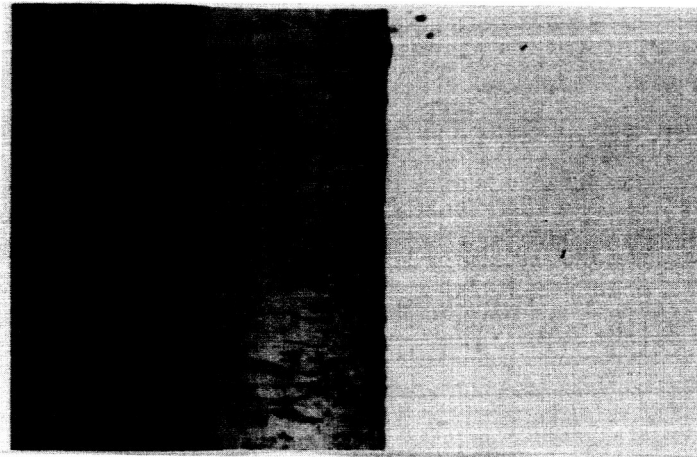


Figure 6. As-Deposited Tantalum on Wrought Iridium.
Mag. 500 X N-6542

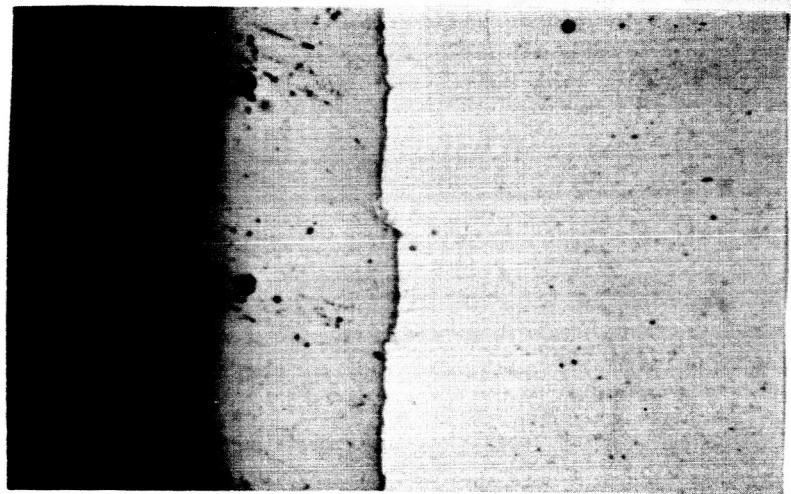


Figure 7. As-Deposited Columbium on Wrought Iridium.
Mag. 500 X N-6816

Figures 8 and 9 show the tantalum-iridium interface after vacuum annealing for four hours at 1350°C and 1700°C, respectively. The width of the visible diffusion zones were approximately seven microns at 1350°C and 31 microns at 1700°C. These values compare with that reported by Passmore⁽¹¹⁾ for a tantalum-iridium couple exposed for four hours at 1700°C. He measured a zone width of 40 microns.

Figure 8. Interface between Electrodeposited Tantalum on Left and Wrought Iridium on Right after Four Hours at 1350°C. Mag. 500 X, N-6543

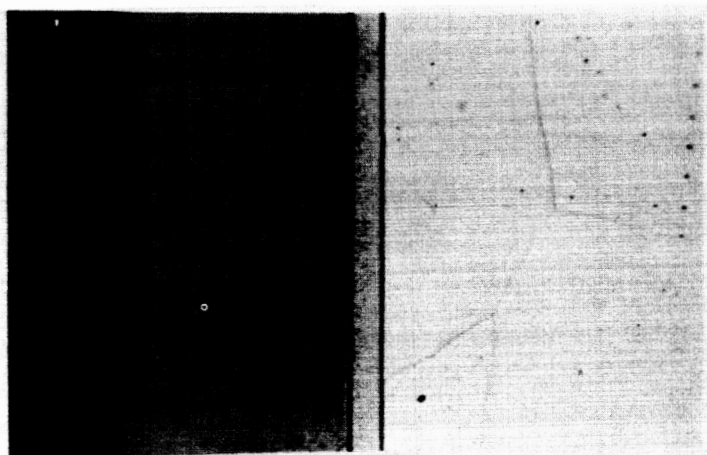
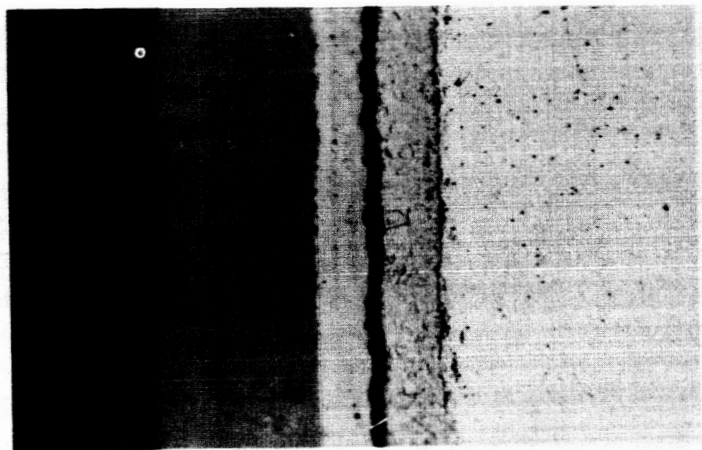


Figure 9. Interface between Electrodeposited Tantalum on Left and Wrought Iridium on Right after Four Hours at 1700°C. Mag. 500 X, N-6544



Microhardness measurements of both the iridium and tantalum near the interface were not sufficiently sensitive to reveal the extent of the solid solution region. By noting the location of the original interface, tantalum apparently diffuses much more rapidly into iridium than iridium into tantalum at 1350°C. At 1700°C, the diffusion rates appear comparable.

Figures 10, 11, and 12 show the columbium-iridium interface after vacuum annealing for four hours at 1350°C, for eight hours at 1350°C, and for four hours at 1500°C, respectively. The width of the visible diffusion zone increased from approximately 8.5 microns to approximately 16.5 microns by doubling the time at 1350°C. Four hours at 1500°C produced a zone of approximately 39.4 microns. Again, our data compare with that of Passmore⁽¹¹⁾ who measured a zone width of 50 microns after four hours at 1700°C.

All of the columbium- and tantalum-plated iridium specimens just described were microbend tested after high temperature exposure. (With the refractory metal coated on iridium, the latter was not exposed to the maximum bending stress which was developed in the outer most layer.) Both of the tantalum-iridium specimens failed after very small deflection (less than five degrees.) Cracks initiated in the diffusion zone of the specimen annealed at 1350°C (see Figure 13.) These cracks propagated into and along the iridium grain boundaries as the bend angle was increased. The specimen annealed at 1700°C also failed after only a small deflection, but crack propagation was so rapid that its origin was not observed. Cracking very likely initiated at the tantalum surface, the point of maximum stress (Figure 14), for several cracks were observed in the tantalum that did not extend into the diffusion zone. The usual ductility associated with unalloyed tantalum was absent, possibly as a result of the extreme grain growth which occurred at 1700°C.

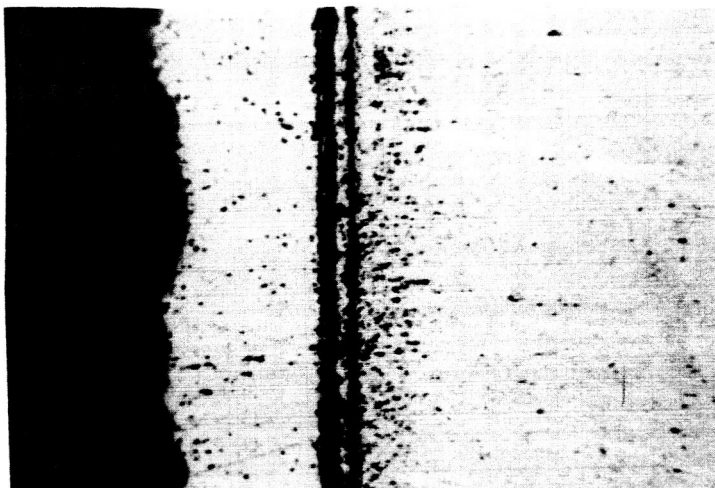


Figure 10. Interface
between Electro-
deposited Columbium
on Left and Wrought
Iridium on Right after
Four Hours at 1350°C.
Mag. 500 X
N-6817

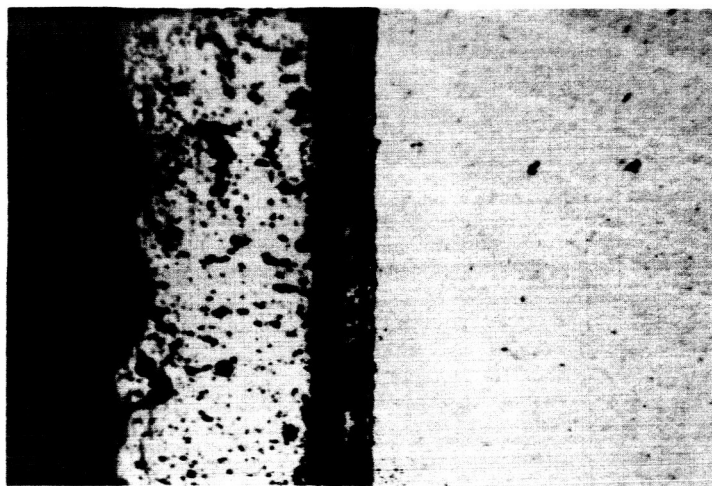


Figure 11. Interface
between Electro-
deposited Columbium
on Left and Wrought
Iridium on Right after
Eight Hours at 1350°C.
Mag. 500 X
N-6818



Figure 12. Same
Couple after Four
Hours at 1500°C.
Mag. 500 X
N-6819



Figure 13. First Sign of Failure during Microbend Test of Tantalum-Plated Iridium Annealed Four Hours at 1350°C. Tantalum and Maximum Bending Stress Are at Left. Mag. 500 X, N-6823

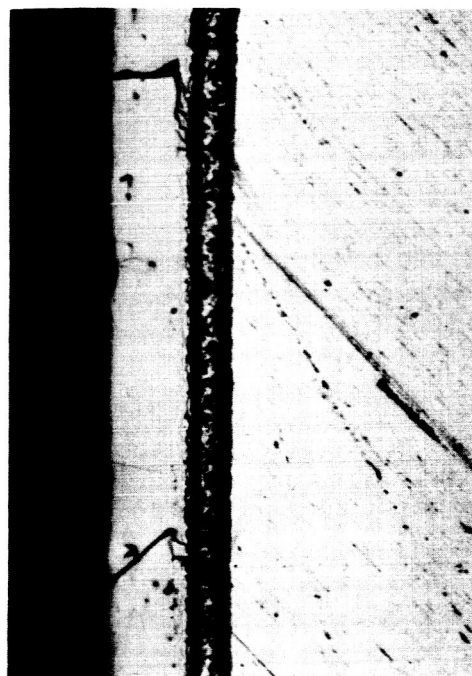


Figure 14. First Sign of Failure during Microbend Test of Tantalum-Plated Iridium Annealed Four Hours at 1700°C. Tantalum and Maximum Bending Stresses Are at Left. Mag. 250 X, N-6824

The columbium-iridium specimens failed after only small deflections. A crack initiated at the surface of the columbium and propagated into the diffusion zone of the specimen annealed four hours at 1350°C. The photomicrograph shown in Figure 15 was taken at the first sign of failure. First signs of failure in the specimens annealed eight hours at 1350°C and four hours at 1500°C are shown in Figures 16 and 17. In both cases, cracks initiated in the diffusion zone and then propagated into the iridium. All specimens failed at bend angles of less than ten degrees.

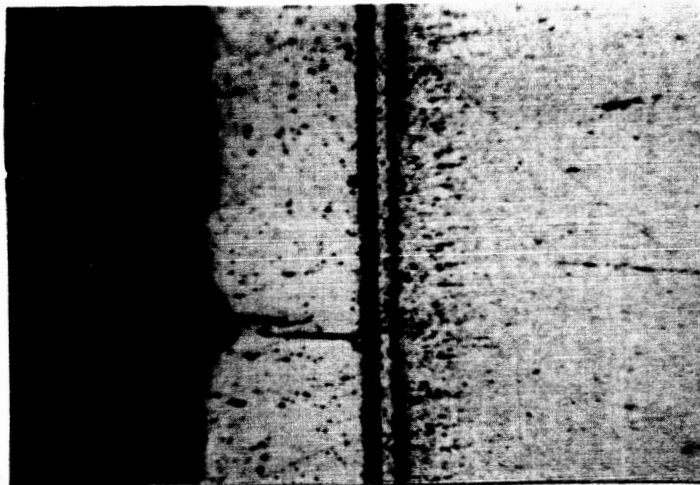


Figure 15. First Sign of Failure during Microbend Test of Columbium-Plated Iridium Annealed Four Hours at 1350°C. Columbium and Maximum Blending Stress Are at Top. Mag. 500 X, N-6820



Figure 16. First Sign of Failure during Microbend Test of
Columbium-Plated Iridium Annealed Eight Hours
at 1350°C. Mag. 500 X, N-6821

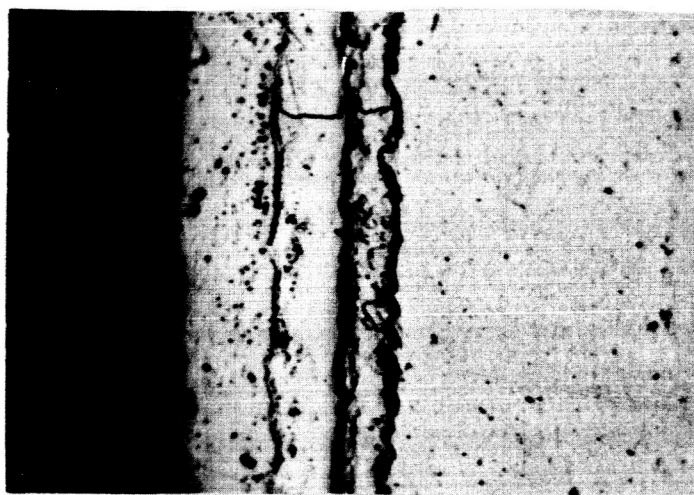


Figure 17. First Sign of Failure during Microbend Test of
Columbium-Plated Iridium Annealed Four Hours
at 1500°C. Mag. 500 X, N-6822

Roll and Pressure Bonding

Figures 18 and 19 (photomicrographs of the roll bonded interfaces between Ta-Ir and Cb-Ir, respectively) show void-free bonds with no apparent diffusion zones formed as a result on hot rolling at 1200°C. These specimens will be annealed and tested in flexure to compare performance with composites formed by the other methods.

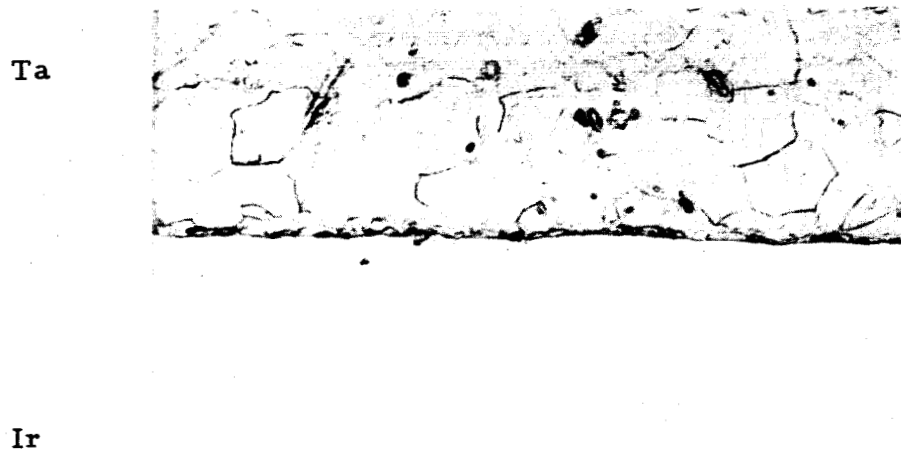


Figure 18. Roll-Bonded Iridium to Tantalum Reduced 25 Per Cent in Thickness at 1200°C. Mag. 500 X, N-6790

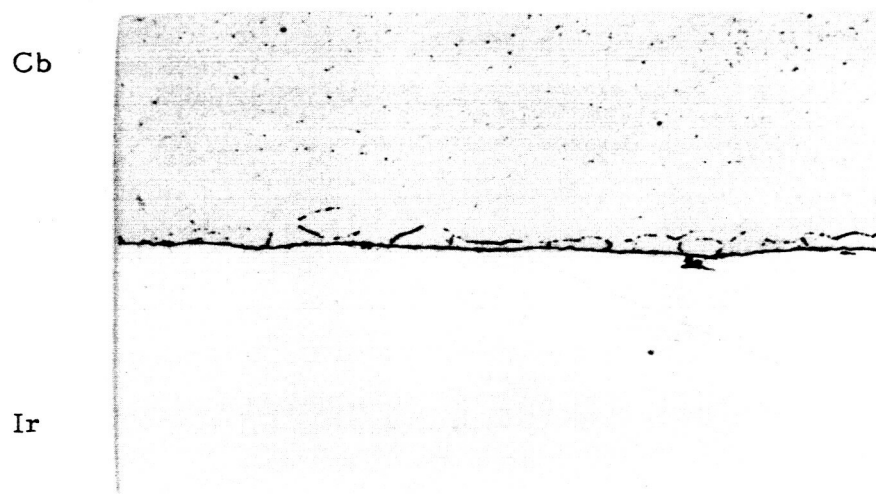


Figure 19. Roll-Bonded Iridium to Columbium, Reduced 25 Per Cent in Thickness at 1200°C, Mag. 500 X, N-6789

One hour at 1500°C produced a good pressure bond between iridium and tantalum with a diffusion zone about 12 microns thick. The iridium-columbium pressure bond failed during disassembly of the clamp, as did the clamp. The technique appears useful for the study of potential barrier layers, but the clamp should be machined from an alloy such as Mo - $\frac{1}{2}$ Ti in order to retard embrittlement.

FUTURE PLANS

With the electrodeposition bath consistently producing iridium coatings, effort will now be directed toward establishing the ductility and adherence of the as-deposited and heat-treated coatings. Finally, limited oxidation and thermal cycling tests will provide sufficient information to assess the value of using iridium on tantalum and columbium for oxidation protection.

The magnitude of damage caused by the interaction of the coating and substrate at elevated temperature will be examined. The benefit derived from a diffusion barrier placed between the iridium coating and substrate will also be considered.

Union Carbide Corporation

Carbon Products Division

Parma, Ohio, February 23, 1965

REFERENCES

1. Criscione, J.M.; et al.: High Temperature Protective Coatings for Graphite. Union Carbide Corporation for Air Force Materials Laboratory, under AF 33(657)-11253, ML-TDR-64-173, Part II, October 1964.
2. Krier, C.A.; and Jaffee, R.I.: Journal of the Less Common Metals. Vol. 5, 1963, pp. 411-431.
3. Phillips, W.L.: Oxidation of the Platinum Metals in Air. ASM Transactions Quarterly, March 1964, pp. 33-37.
4. High Temperature Materials Program. General Electric FPLD, Progress Report 17A, October 1962.
5. Buchinski, J.J.; and Girard, E.H.: Study of Ductile Coatings for the Oxidation Protection of Columbium and Molybdenum Alloys. Metals and Controls, Inc. for Bureau of Naval Weapons under NOw 63-0706-c, Final Report, October 1964.
6. Fryburg, G.C.; and Petrus, H.M.: Kinetics of the Oxidation of Platinum. J. Electrochem. Soc., Vol. 108, No. 6, June 1961, pp. 496-503.
7. Perkins, R.A.: Coatings for Refractory Metals. Proceedings of 1964 Golden Gate Metals Conference, San Francisco, Materials Science and Technology for Advanced Applications, Vol. II, p. 579.
8. Norton, F.J.: Nondiffusibility of Oxygen Through Platinum. J. Appl. Phys. 29, 7, July 1958, p. 1122.
9. High Temperature Materials Program. General Electric NMPO under Contract No. AT-(40-1)-2847, July 1962.
10. Betteridge, W.; and Rhys, D.W.: The High-Temperature Oxidation of the Platinum Metals and Their Alloys. First International Congress on Metallic Corrosion, 1961, pp. 186-192.
11. Passmore, E.M.; et al.: Investigation of Diffusion Barriers for Refractory Metals. ManLabs, Inc. for Aeronautical Systems Division, under AF 33(616)-6354, ASD-TDR-62-432, July 1962.
12. Withers, J.C.; and Ritt, P.E.: Iridium Plating and Its High Temperature Oxidation Resistance. Proceedings of the American Electroplaters Society, 1957, pp. 124-129.
13. Mellors, G.W.; and Senderoff, S.: Electrodeposition of Coherent Deposits of Refractory Metals. Electrochemical Society Abstract No. 89, October 1963.

REFERENCES (Continued)

14. Mellors, G. W.; and Senderoff, S.: The Electroforming of Refractory Metals. Plating, October 1964.
15. Flinn, R. A.; and Trojan, P. K.: Examination of Microstructure under Varying Stress. Metals Progress, July 1955.

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